PROGRESS IN KINETIC THEORY:

GENERALIZATIONS OF BOLTZMANN'S EQUATION

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ABSTRACT

We have recently celebrated the hundredth birthday of Boltzmann's kinetic equation, an equation that has been enormously fruitful in physics and engineering. However, Boltzmann's model of transport processes has its limitations. It is based upon a view of Nature that is 'coarse-grained' in time and space, the intervals of coarse-graining being the duration of a collision, and the range of intermolecular force. In the coarse-grained world of rarefield systems, Boltzmann's Stosszahlansatz works well. As more data on transport processes in liquids and dense gases accumulate, the need for systematic generalization of Boltzmann's equation (and the Chapman-Enskog analysis) grows. Computer experiments, neutron scattering experiments, and the scattering of laser beams have been particularly stimulating here, for they probe extremely short intervals of space and time in the dynamics of the target system. Coarse-graining, and the

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[*]Professor of Applied Physics. This research was sponsored in part by the National Science Foundation.

[†]Paper presented at 10th International Symposium on Rarefied Gas Dynamics; Snowmass, Colorado, July 18-23, 1976.

Stosszahlansatz are no longer acceptable. It is not widely appreciated that for the past decade, scientists have had a compact and elegant formalism at their disposal, for the construction of generalized kinetic equations. The new equations describe the response of the N-body system in the full frequency and wave-number domain. They are characterized by kernels that exhibit both spatial and temporal 'memory' and are, necessarily, very complicated. We shall review recent progress in the analysis, commenting on 1) the generalization of Boltzmann's equation to higher densities . . . the cluster expansion and the Bogoljubov Ansatz, revisited. 2) the generalized kinetic equations of Zwanzig and Mori 3) progress in analysis and solution.

I. INTRODUCTION

Ludwig Boltzmann proposed his remarkable equation in a paper published in 1872, a little over a century ago. Centennial celebrations have been held in Vienna, in Providence, and, doubtless, elsewhere. The equation and the point of view that it represents have been enormously fruitful for physics and engineering. Yet, the equation occupies an unusual place in kinetic theory; it is easy to derive in a heuristic, 'hand-waving' manner, but its proper derivation requires long and subtle argument. Thus, its generalization is difficult, and its precise range of validity uncertain. Progress in this aspect of kinetic theory has generally been slow and quiet. But, the last decade has been different. New mathematical formalisms have been brought to bear and we are much closer to an understanding of the kinetic theory of relatively dense systems. I shall

try to describe some of the recent progress in this paper. No one interested in rarefield gas dynamics can fail to respond to the challenge of higher densities. The challenge is set not merely by a fascinating problem in mathematical physics, but, more to the point, by phenomena and data demanding explanation.

We shall write Boltzmann's equation as

$$\frac{\partial}{\partial t} f(\underline{r}, \underline{p}, t) + \frac{1}{m} \underline{p} \cdot \frac{\partial}{\partial \underline{r}} f = J(f, f) \quad . \tag{1}$$

Its linear version is:

$$\frac{\partial}{\partial t} h(\underline{r}, \underline{p}, t) + \frac{1}{m} \underline{p} \cdot \frac{\partial}{\partial \underline{r}} h = \int d^3\underline{p}' \, K(\underline{p}, \underline{p}') \, h(\underline{r}, \underline{p}', t) \tag{1a}$$

where

$$f(\underline{r}, \underline{p}, t) = n M(\underline{p}) \, (1 + h(\underline{r}, \underline{p}, t))$$

and $M(\underline{p})$ is the normalized Maxwellian for temperature T. We shall sometimes use the dimensionless momentum $\underline{\xi}$, $\underline{p} = mv_0 \underline{\xi}$, with $v_0^2 = k_B T/m = 1/m\beta$. Otherwise the notation is standard.

The left-hand side of Eqs. (1) is unobjectionable. It is the right-hand side, Boltzmann's famous collision term, that expresses "the physics." We know, for example, that $M(\underline{p}) K(\underline{p}, \underline{p}')$ is symmetric, and that K is unaltered by simultaneous rotation of $\underline{p}$ and $\underline{p}'$. Further, K has five eigenfunctions, degenerate with respect to eigenvalue zero. These functions are the collisional invariants $(1, \underline{p}, p^2)$. Particularly convenient is the orthonormal set:

$$\psi_1 = 1 \qquad \psi_2 = \xi_3$$

$$\psi_3 = \frac{1}{\sqrt{6}}(\xi^2 - 3) \qquad \int d^3\underline{p}\, M(\underline{p})\, \psi_\alpha \psi_\beta = \delta_{\alpha\beta} \qquad (2)$$

$$\psi_4 = \xi_1 \qquad \psi_5 = \xi_2$$

(Note that the kinetic energy, rather than the total energy, is conserved.) This brings us to the most important feature of the collision term, so obvious that it is usually ignored in textbooks; the change in the distribution function due to interactions is expressed in terms of 'collisions per unit time'. An element of 'coarse-graining' is thereby introduced into the description of Nature. Should a characteristic time, t_o, be associated with collisions near equilibrium, and this time be compounded of the range of force r_o and a thermal velocity, v_o, then $f(\underline{r}, \underline{p}, t)$, the solution to Eqs. (1, 2) will have meaning only for $t \gg t_o$. Otherwise, the relation between Boltzmann's $f(\underline{r}, \underline{p}, t)$ and the one-particle distribution function $f_1(\underline{r}, \underline{p}, t) = \left\langle \sum_i \delta^3(\underline{r} - \underline{q}_i(t))\, \delta^3(\underline{p} - \underline{p}_i(t)) \right\rangle$ is not simple. What, for example, is the relation between $f_1(\underline{r}, \underline{p}, t=0)$ and $f(\underline{r}, \underline{p}, t=0)$?

A second feature of the collision term is its form, an expression of the 'Stosszahlansatz'. Correlations in position and velocity of the colliding particles are ignored, and a two-particle distribution function is approximated by the product of one-particle functions. The approximation is reasonable when the gas is dilute. Then, another set of scales appears, t_1, the mean time between collisions and r_1, the mean free path. Boltzmann's equation is accurate in these regimes. As the system becomes denser, $t_1 \to t_o$, $r_1 \to r_o$, and well-known difficulties appear.

Finally, we note that the collision term, giving the "average number of collisions per unit time" causes f to be interpreted as an average

density. But, where is the equation that determines fluctuations in density? In Boltzmann's formulation the 'noise' that turns out to be so rich in information, is absent. Thus, there are three issues we must deal with: the coarse-graining, the restriction to low density, and the question of fluctuations. (One aspect is: are the approximations independent? Does one imply another?)

The modern theory, which we shall describe ahead, responds to these questions. It is quite general, and is in no way limited to certain ranges of time-interval, space-interval, or density. It is also quite abstract. We shall approach it gradually by reviewing attempts, now 'classical', to improve upon Boltzmann. Finally, we confront the key question: How valuable are the new insights?

II. QUASI-CLASSICAL KINETIC THEORY

An important goal of kinetic theory is the calculation of transport coefficients. The classical approach, based upon the Chapman-Enskog analysis of the Boltzmann equation, is well-known. In this section, I shall present a typical coefficient, the shear viscosity, in the modern manner. The techniques and attitudes introduced here will reappear later in more complicated situations. Further, even in this simple case, they present the functional assumptions of Chapman, Enskog, and Bogoljubov, and the notions of time-scaling in a different light.

The formulation of kinetic theory in a Hilbert space of phase functions (dynamical variables) or field functions (distribution functions), and the introduction of operators into the space, characterizes the 'modern'

approach. Thus, classical dynamics is made to resemble quantum dynamics. The ingenious use of the simplest operators, the projection operators, further marks the approach.

We ask for the manner of relaxation of a typical Fourier component of $h(\underline{r},\underline{p},t)$ when a Boltzmann gas is slightly perturbed from equilibrium. The initial value problem has the form:

$$\left(\frac{\partial}{\partial t} + \frac{i}{m}k\cdot\underline{p} - K\right)h(\underline{k},\underline{p},t) = \left(\frac{\partial}{\partial t} - H(k)\right)h(\underline{k},\underline{p},t) = 0,\ h(\underline{k},\underline{p},0)\ \text{given} \qquad (3)$$

and we know that the resolvent operator,

$$G(\underline{k}) = (s - H(k))^{-1}\ ;\ s\ \text{complex}$$

is crucial. The operator H has a point spectrum and a continuous spectrum, which, for reasonable potentials, and small k, are disjoint. The 'hydrodynamic' points (poles), i.e., those which approach zero as $k \to 0$, are of particular interest. Now consider the Hilbert space of functions of $\underline{p}$ with the norm suggested by Eq. (2) $(\psi_\alpha, \psi_\beta) = \delta_{\alpha\beta}$. Introduce P, the projector onto the space spanned by the ψ_α, and $Q = 1 - P$, its complement. The resolvent becomes:

$$\frac{1}{s - H} = \frac{1}{s - HQ} + \frac{1}{s - HQ}HP\frac{1}{s - H} \qquad (4)$$

and its matrix elements in the sub-space satisfy the equation

$$\langle\alpha|G|\beta\rangle = \frac{1}{s}\delta_{\alpha\beta} + \sum_{\alpha'}\langle\alpha|\frac{1}{s - HQ}|\alpha'\rangle\langle\alpha'|G|\beta\rangle \quad . \qquad (5)$$

The projection of $h(\underline{k},\underline{p},t)$ into the subspace is important because the components (ψ_α, h) are the hydrodynamical moments, from which one

forms the equations of fluid dynamics. Thus, we expect expressions for the transport coefficients to lurk among the $\langle \alpha | G | \beta \rangle$. We shall extract the viscosity. To begin, notice that the behavior of H and the ψ_α upon rotation and reflection causes many of the matrix elements $\langle \alpha | \cdots | \alpha' \rangle$ in Eq. (5) to vanish. For example, if we take $\underline{k}$ to be parallel to the 3-axis, all off-diagonal elements in the fourth and fifth rows of $\langle \alpha | G | \beta \rangle$ vanish. The function $\langle 4 | G | 4 \rangle = \langle \xi_1 | G | \xi_1 \rangle$ describes the relaxation of transverse momentum. The 'collapse' of the sum in Eq. (5) causes it to have the simple form:

$$\langle 4 | G | 4 \rangle = \frac{1}{s - D'(\underline{k}, s)} \tag{6}$$

$$D'(\underline{k}, s) = \langle 4 | HQ \frac{1}{s - QHQ} QH | \rangle$$

$$= -k^2 v_o^2 \quad \langle \xi_1 \xi_3 | Q \frac{1}{s - QHQ} Q | \xi_1 \xi_3 \rangle$$

$$= -k^2 v_o^2 \quad \langle \xi_1 \xi_3 | \frac{1}{s - K + \frac{i}{m} Qk \cdot pQ} | \xi_1 \xi_3 \rangle$$

(We have used the relations $Q \frac{1}{s-HQ} = Q \frac{1}{s-QHQ}$, $P \xi_1 \xi_3 = 0$, and $QKQ = K$, to reach the final equation.)

We expect to see the linearized Navier-Stokes equation for the transverse momentum in Eq. (6), and indeed it appears as the limit $k \to 0$ is taken in $D'(\underline{k}, s)$. Thus

$$\langle 4 | G | 4 \rangle \to \frac{1}{s - \frac{1}{mn} \eta k^2} \tag{7}$$

with

$$\eta = n k_B T \quad \langle \xi_1 \xi_3 | \frac{1}{K} | \xi_1 \xi_3 \rangle$$

The expression for η involves the solution of an integral equation. It is precisely the Chapman-Enskog result. The remaining three-by-three matrix yields the longitudinal eigenvalues, two damped sound modes, and a mode describing the diffusion of heat. The Chapman-Enskog expression for λ, the coefficient of heat diffusion, may be read out of the dispersion relation. Thus, the projection-operator treatment is equivalent to the traditional. No hypothesis about 'normal solutions', in which the time-dependence enters only through the moments, need be made. Hydrodynamical behavior is associated with the smallest eigenvalues (and eigenvectors) of a scattering operator which describes dynamics on a finer scale of space and time. The expansion in wave-vector, $\underline{k}$, gives a series in the ratio of mean free path to characteristic macroscopic dimension of the system. When this ratio is small, the hydrodynamical eigenvalues are well separated from the higher eigenvalues and the continuous spectrum. Then, there is an epoch $t > t_2 > t_1$ during which the distribution function does indeed relax in the manner of its moments. The modern picture is overall, clearer.

Equation (7) contains a bonus. We may write it as:

$$\eta = n\underline{k}_B T \lim_{s \to 0} \int_0^\infty dt\, e^{-st} \int d^3\underline{p}\, M(\underline{p})\, \xi_1 \xi_3\, e^{-tK} \xi_1 \xi_3 \quad . \tag{8}$$

This has the form of a Green-Kubo relation, giving a transport coefficient in terms of an auto-correlation function. Of course, Eq. (8) is somewhat synthetic, and does not truly express a 'fluctuation-dissipation theorem' for, at the Boltzmann level, we do not discuss exact dynamics. The relevant dynamical variable here is the (1, 3) component of the pressure tensor. However, only the kinetic portion $\xi_1 \xi_3$ appears here — an expression

of the limitations of Boltzmann's equation. We shall have more to say about Eq. (8) later.

III. SIGNIFICANT, AND PARTIALLY SUCCESSFUL APPROACHES

The success and efficiency of the projection operator technique would suggest that we apply it in a more complicated context. We shall, in Section IV. This section, III, may be regarded as an interlude, in which we summarize progress in a mixed line of research. Mixed because on the one hand it deals with the Liouville equation, the full dynamics, but on the other hand it concerns itself principally with corrections to the Boltzmann equation and to transport coefficients. These corrections turn out to be of successively higher order in density. We shall be brief here, because most of the following has already achieved 'textbook' status.

Thus, in order to correct and understand Boltzmann's equation, we must begin at the beginning, with exact dynamics. We contemplate the motion of a dynamical variable $A(t) = A(\underline{q}_1(t), \cdots \underline{q}_N(t); \underline{p}_1(t), \cdots \underline{p}_N(t)) = A(\underline{q}_1{}^o, \cdots \underline{p}_N{}^o; t)$ and the motion of the phase-space density, $f_N(\underline{r}_1, \cdots \underline{p}_N; t)$. Thus,

$$\frac{d}{dt} A = [A, H] = iLA$$

$$\frac{\partial}{\partial t} f_N = -iLf_N \qquad f_N(t=0) = f_N(0) \tag{9}$$

where operator iL symbolizes 'Poisson-bracketing with the Hamiltonian'. For the systems we consider,

$$iL\, f = \sum_j \left(\frac{1}{m} \underline{p}_j \cdot \frac{\partial f}{\partial \underline{r}_j} + \underline{F}_j \cdot \frac{\partial f}{\partial \underline{p}_j} \right)$$

for a field-function. It has the same form, with $\underline{r}_k \to \underline{q}_k$, when operating upon a dynamical variable. Finally, we note a typical connection,

$$f_N(\underline{r}_1 \cdots \underline{p}_N ; t) = \left\langle \delta^3(\underline{r}_1 - \underline{q}_1(t)) \cdots \delta^3(\underline{p}_N - \underline{p}_N(t)) \right\rangle_o$$

between distribution function (field function) and the appropriate dynamical variable. The averaging is with respect to the initial ensemble, $f_N(0)$.

The dynamical variable

$$\hat{f}_1(\underline{r},\underline{p},t) = \sum_{j=1}^{N} \delta^3(\underline{r} - \underline{q}_j(t))\ \delta(\underline{p} - \underline{p}_j(t)) \quad , \tag{9a}$$

and its Fourier transform

$$\hat{f}_1(\underline{k},\underline{p},t) = \sum_{j=1}^{N} e^{-i\underline{k}\cdot\underline{q}_j(t)}\ \delta^3(\underline{p} - \underline{p}_j(t)) \quad ,$$

are of special interest to us; $\left\langle \hat{f}_1(\underline{r},\underline{p},t) \right\rangle_o$ is the one-particle distribution function and the equilibrium correlation function is related to the observed neutron scattering law $S(\underline{k},\omega)$, through $\delta\hat{f}_1 = \hat{f}_1 - \left\langle \hat{f}_1 \right\rangle_{eq}$, and

$$S(\underline{k},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\ e^{-i\omega t} \int d^3\underline{p}\, d^3\underline{p}'\ \left\langle \delta\hat{f}_1^*(\underline{k},\underline{p}',0)\ \delta\hat{f}_1(\underline{k},\underline{p},t) \right\rangle_{eq} \tag{9b}$$

Reduced distribution functions for the N-particle system play an important rôle. In particular, they satisfy a hierarchy of equations (moment-equations) of which only the first concerns us here. It is

$$\left(\frac{\partial}{\partial t} + \frac{1}{m}\underline{p}_1 \cdot \frac{\partial}{\partial \underline{r}_1}\right) f_1(\underline{r}_1,\underline{p}_1,t) = -\frac{\partial}{\partial \underline{p}_1} \cdot \int d^3\underline{r}_2\, d^3\underline{p}_2\, F_{12}\, f_2(\underline{r}_1,\underline{r}_2;\underline{p}_1,\underline{p}_2;t) \ . \tag{10}$$

While the right hand side of Eq. (10) describes the change in f_1 due to collisions, the equation is far from Boltzmann's. A conservative view would see it merely as a connection between first and second moments.

The search for a true, closed, Master equation:

$$\left(\frac{\partial}{\partial t}+\frac{1}{m}\underline{p}_1\cdot\frac{\partial}{\partial \underline{r}_1}\right)f_1 = \Phi(\underline{r}_1,\underline{p}_1;f_1;t)$$

has, for many decades, been a search for the philosophers' stone. Like the stone, it cannot exist, but in searching for it one finds much that is valuable.

In his important book 'Dynamical Problems in Statistical Physics', N. N. Bogoljubov presented an approach to the problem of the Master Equation that stimulated a decade of research activity in the West. Its essence is that a Master equation does exist, for the epoch $t > t_o$, and that its form is based upon the Ansatz that

$$f_s(\underline{r}_1 \cdots \underline{p}_s;\ t) = f_s(\underline{r}_1 \cdots \underline{p}_s;\ f_1(\underline{r}_1,\underline{p}_1;t)) \qquad s \geq 2.$$

and upon a rather curious initial condition. Thus, after a collision time, more-or-less, the higher distribution functions 'slave to' f_1 in their temporal behavior. The closed Master (kinetic) equation is then:

$$\left(\frac{\partial}{\partial t}+\frac{1}{m}\underline{p}_1\cdot\frac{\partial}{\partial \underline{r}_1}\right)f_1 = \Phi_1(\underline{r}_1,\underline{p}_1;f_1) \qquad (11)$$

Unfortunately, we do not know the explicit form of $f_2(\ ;f_1)$, and we do not know the correct initial condition to be used with Eq. (11). Further approximation is necessary before an explicit theory can be developed. However, it is possible to go directly to the hydrodynamic stage with Eq. (11) by adopting the strategy of Chapman and Enskog. The normal solution, wherein f_1, in turn, 'slaves to' the slow, temporal evolution of its moments, is introduced (projection onto hydrodynamical sub-space) and expansion is made with respect to smallness of spatial variation of the moments (expansion in powers of $\underline{k}$). The integral equations which result are complicated,

but, in principle, a solution exists. Unfortunately, the kernels are not known explicitly.

Explicit evaluation of Eq. (11) has, to date, only been carried out through expansion with respect to density. In fact, a systematic expansion in the density (of a uniform reference state), coupled with an unhappy assumption about the initial state, viz.

$$f_s(r_1, \cdots p_s; 0) = \prod_{i=1}^{s} f_1(r_i, p_i; 0)$$

will close the hierarchy, and, in particular Eq. (10). The final forms are the same, whether the Bogoljubov Ansatz is made, or not. The technique is that of cluster-expansion, similar to the Ursell-Mayer technique of equilibrium statistical mechanics. With $(\underline{r}_i, \underline{p}_i)$ denoted x_i, one has

$$\begin{aligned} f_2(x_1 x_2; t) &= f_2^{(o)}(x_1 x_2; t) + n\, f_2^{(1)}(x_1 x_2; t) + \cdots \quad ; \\ f_2^{(o)}(x_1 x_2; t) &= S_t^{(2)}(x_1 x_2)\, f_1(x_1; t)\, f_1(x_2; t) \\ f_2^{(1)}(x_1 x_2; t) &= \int dx_3\, S_t^{(3)}(x_1 x_2 x_3)\, f_1(x_1; t)\, f_1(x_2; t)\, f_1(x_3; t) \end{aligned} \tag{12}$$

The $S_t^{(k)}$ appearing in Eq. (12) are symbolic operators, which refer to the motion of k particles. For example, $S_t^{(3)}(x_1 x_2 x_3)$ alters the phases which appear in $f_1 f_1 f_1$ in a well-defined manner, based upon the motion of one, two, and three-particle groups (clusters) in the time interval, t. Connection with the Boltzmann equation is made by replacing $S_t^{(k)}$ by $S_\infty^{(k)}$, and by neglecting the difference in position of colliding molecules (coarse-graining). Finally, one has

$$\left(\frac{\partial}{\partial t}+\frac{1}{m}\underline{p}_1 \cdot \frac{\partial}{\partial \underline{r}_1}\right)f_1 = n\,\overline{J}(f_1 f_1) + n^2\,K(f_1 f_1 f_1) + \cdots \qquad (13)$$

with or without the Ansatz.

The three-body term and its implications for thermodynamics and hydrodynamics have received considerable attention. The second virial coefficient appears correctly in the equilibrium distribution, and corrections to η and λ have been computed for a gas of hard spheres. However, attempts to continue the series in density have led to unpleasant surprises. In three dimensions, the four-body and all higher order terms diverge, while in two dimensions, the three-body and higher order terms diverge. The cluster-Bogoljubov approach seems to have come to a dead end.

It is difficult to estimate just how much truth the cluster theory contains. Is it true only in the limit $t \to \infty$, or can the system of Eq. (12) tell us something about the approach to the hydrodynamic stage in a moderately dense gas? Is the natural variable for expansion some combination of time and density? How much has been lost in making the crude approximation of the initial condition? How does one surmount the density-divergence? Can the singular terms in the expansion of η and λ (which turn out to be $\sim n^2 \log n$) be seen in experiment? These questions have not yet been answered throughly.

If one restricts oneself to transport coefficients, one can arrive at the same point more directly, in a manner that shows that some of our concerns are irrelevant. The calculation is based upon the Green-Kubo expressions, themselves based upon a linear-response theory (small perturbation from equilibrium) that is palatable. One has, for example,

$$\eta = \frac{1}{k_B T V} \lim_{s \to \infty} \left\langle T_{13} \left| \frac{1}{s - iL} \right| T_{13} \right\rangle \qquad (14)$$

T_{ij} being the pressure tensor, and the density-expansion is generated by an expansion of the resolvent called the 'binary-collision expansion'. As in our Eqs. (7) and (8), the Kubo and Chapman-Enskog methods lead to the same results. The same divergences appear; it is clear that they have nothing to do with choice of initial condition or with coarse-graining. The theory based upon Eq. (14) is 'exact', and it yields the same transport coefficients (whenever the results are finite) as do the Boltzmann and generalized Boltzmann theories, which are coarse-grained. How do we avoid paradox? Perhaps by asserting that the true smallness-parameter for expansion involves n and t in such a way that it is small only for n small and t large. Another possible clue is: the Laplace transforms of autocorrelation functions associated with transport coefficients have been found to be singular at $s = 0$. A subsequent expansion in density only makes the non-analyticity clearer.

In any case, Boltzmann's equation appears as the 'leading term' in a formal expansion of the exact dynamics, with respect to density. There is another expansion, worth investigating, and that is in terms of the strength of forces between the particles. The expansion is limited in its applicability to the physical world because it requires that the potential be bounded, or most weakly-divergent. Then, the expansion may be thought of as equivalent to an expansion in inverse temperature. When Boltzmann's equation is expanded in this manner one obtains a kinetic equation, first analyzed by Landau. If one does not first expand in density, but expands the exact dynamics in terms of coupling strength, one obtains a system

that should illuminate the issues of convergence, initial conditions, etc., raised above. The leading term is a kinetic equation of generalized Fokker-Planck form. It is of some use in plasma physics, and we shall meet it again.

Finally, we turn to the question of fluctuations. There is no such issue in the exact dynamics of an N-body system. It is only when one contracts, or coarsens the description that problems arise. Except for special cases, the contracted system is not in itself closed. Strictly speaking, a 'noise' term is always present, for the degrees of freedom, or time-scales, 'projected out' can never be completely eliminated. The effect of the noise is usually small; hence our ability to invoke macroscopic or microscopic physics to describe Nature. The study of critical phenomena is a popular counter-example.

To restore the noise-term to Boltzmann's equation, in the absence of a systematic theory, is an exercise in informed guess-work. The paradigm is Langevin's equation for the momentum of a macroscopic particle,

$$\frac{dp}{dt} + \frac{\gamma}{m} p = F(t)$$

$$\frac{d}{dt}\langle p\rangle + \frac{\gamma}{m}\langle p\rangle = 0 \qquad \langle F\rangle = 0 \tag{15}$$

$$\langle F(t)F(s)\rangle = 2Q\,\delta(t-s) \;\; ; \;\; F \text{ is Gaussian.}$$

The equation for the test particle coupled to its N-1 colleagues is replaced by an equation for a single momentum, driven by a 'stochastic' force, and damped by a macroscopic force. The equation for the averaged momentum is the analog of Boltzmann's equation. The success of the Langevin equation

in describing correlated fluctuations, etc., is based upon a crucial point of time scaling — that the correlation time for fluctuations is much shorter than the macroscopic relaxation time. Hence, the delta function in Eq.(15). The time-scaling argument, while reasonable, is quite difficult to prove. It can only describe a limiting case. As a final point of physics, a 'fluctuation-dissipation theorem' connects the amplitude of the force with γ. It reflects the fact that the test particle, whatever its initial state, comes to equilibrium with the 'bath' of N-1 other particles.

We shall describe two slightly different approaches to the construction of the 'correct' Boltzmann-Langevin equation. Both lead to the same equation, then, via Chapman-Enskog, to equations for fluctuating hydrodynamics that are now classic, and have some practical significance. The proper fluctuating quantity is $h(\underline{r},\underline{p},t)$ of Eq. (1a). Since $(\underline{r},\underline{p})$ may be thought of as labels, the kinetic equation resembles a set of first-order equations for quantities $a_i(t)$, $i = (\underline{r},\underline{p})$, which relax according to

$$\frac{da}{dt}i + \sum_j (A_{ij} + S_{ij})\, a_j = 0 \qquad (16)$$

where A_{ij} is anti-symmetric and S_{ij} symmetric. Here $a_i \leftrightarrow \sqrt{M(\underline{p})}\; h(\underline{r},\underline{p},t)$.

When a stochastic 'force' or noise source, $F_i(t)$, is added to the rhs, and the force function is a Gaussian process with zero correlation time, $\langle F_i(t)\, F_j(s)\rangle = 2\, Q_{ij}\, \delta(t-s)$, we have a not unusual problem in the theory of Gaussian Markov processes. The a_i are also distributed in a Gaussian manner, with $W(a_j)$ proportional to $\exp\left(-\frac{1}{2}\sum_{ij} a_i E_{ij} a_j\right)$. Now, the pieces fall into place. $G_{ij} = A_{ij} + S_{ij}$ is known. The stationary nature of the process gives Q_{ij} in terms of G_{ij} and E_{ij} and the latter is connected with the entropy through the Boltzmann-Einstein relation, $W(a_i)$ proportional to

$\exp\left(\frac{\Delta S(a_i)}{k_B}\right)$. Since the entropy of the distribution may be determined from $f \log f$, the system is closed, and we have a unique prescription for calculating Gaussian forces. One finds that the rhs of Eq. (1a) should be augmented by $F(\underline{r},\underline{p},t)$, where

$$\langle F(\underline{r},\underline{p},t)\, F(\underline{r}',\underline{p}',t)\rangle = 2M^{-1}(\underline{p}')\, K(\underline{p},\underline{p}')\, \delta^3(\underline{r}-\underline{r}')\, \delta(t-t')$$

This approach has been discussed in detail by Fox and Uhlenbeck.

The second approach, due to Bixon and Zwanzig, is somewhat more intuitive, more 'physical'. Instead of adding a noise source to the linearized Boltzmann equation, and thereby changing its nature, these authors regard the equation as the proper average of another equation, which contains fluctuations. The new equation concerns the dynamical variable $\hat{h}(\underline{r},\underline{p}\ ;\ \underline{q}_i(t),\ \underline{p}_i(t))$, which is related to $\hat{f}_1(\underline{r},\underline{p},t)$ through

$$\hat{f}_1(\underline{r},\underline{p},t) = nM(\underline{p})\ (1+\hat{h}(\underline{r},\underline{p},t))\ .$$

One can write a true equation for $\hat{h}$, via $\hat{f}_1$; it involves $\hat{f}_2$ and resembles the first equation of the hierarchy. An equation for $\hat{h}$ follows at once. Bixon and Zwanzig write this equation in the suggestive form: (see Eq. (3))

$$\left(\frac{\partial}{\partial t}+\frac{1}{m}\underline{p}_1 \cdot \frac{\partial}{\partial \underline{r}_1} - K\right)\hat{h} = F$$

where the extremely complicated rhs is taken to be the 'noise'. Its average is assumed to be zero, though it is not, and its correlation time is taken to be zero, though it is not. Yet, to the extent that the linearized Boltzmann equation is a correct description (low densities, low frequencies) these assumptions about the noise are tenable. One has here a theory that is not purely stochastic, that tries to identify the dynamical elements in

the low-density limit.

IV. MODERN THEORIES

The treatments of N-body dynamics sketched above have concentrated upon the later stages of evolution. Some procedure of 'coarse-graining', of eliminating information corresponding to short time, or high-frequencies, is a natural part of the formalism. Indeed, John Kirkwood introduced his method of coarse-graining through an argument that it is an essential part of the measuring process, and therefore needs be an essential part of the mathematical formalism.

Certainly, there is a problem of resolution in every experiment. But the issue is of little import in the experiments which have stimulated the development of modern kinetic theory. These are experiments to determine the 'scattering law' for neutrons interacting with simple fluids and dense gases, experiments in the scattering of intense beams of light, and, most important, computer experiments in which N-body dynamics is simulated. The interpretation of these requires a theory that is good for arbitrary intervals of time and space. Of course, such a theory is impossibly complicated. But, I shall describe a compact formalism that serves as a good platform for leaping to appriximations — in all directions. As promised, it is based upon the ingenious use of projection operators.

As a first example, consider the kinetic equation for a classical 'test-particle'. In the Boltzmann limit, the system approaches the Lorentz model. One has a linear transport equation, resembling Eq. (1a), for $f(\underline{r},\underline{p},t)$. Since only a single conservation law exists, the hydrodynamic

pole is non-degenerate. We begin by returning to the Liouville equation, and denote the N-body distribution function f_N by $\rho(\bullet\bullet; t)$. The test-particle distribution function is related to f_N or ρ through a contraction, or projection. For example,

$$Pf_N = \rho_B \int dx_2 \cdots dx_N f_N = \rho_B f(\underline{r}, \underline{p}, t) \quad , \tag{17}$$

$$= \rho_o V g(\underline{r}, \underline{p}, t)$$

where $$\rho_B = \frac{\rho_o V}{M(\underline{p})} \quad ,$$

and ρ_o is the canonical, equilibrium distribution. Note that $P^2 = P$, as it should, and that the choice of the multiplicative factor in Eq. (17) is not unique.

The key to our analysis is a simple identity, first given by R. W. Zwanzig. If $1 - P$ is denoted by Q, the decomposition $\rho = P\rho + Q\rho$ permits one to formally integrate the Liouville equation to obtain:

$$\left(\frac{\partial}{\partial t} + PiL\right)P\rho = \int_o^t dt \; PiL\, e^{-i\tau QL} QiL\, P\rho(t-\tau) - PiL\, e^{-itQL} Q\rho(0) \tag{18}$$

for <u>any</u> projector, P. Since $P\rho$ is proportional to f, Eq. (18) is, except for the last term, an exact, closed equation for the test-particle density. The last term vanishes only if the distribution is initially in the projected sub-space, i. e., $Q\rho(0) = 0$. This condition is not a spoiler; it admits initial distributions of the form $\rho_o \varphi(1)$, where $\varphi(1)$ is an arbitrary function of $(\underline{r}_1, \underline{p}_1)$. The initial distribution need not be close to equilibrium. Should the condition not be satisfied, one has the interesting problem of determining how long it takes for memory of the initial state to disappear. (Does the Bogoljubov Ansatz ever hold?) Though abstract, Zwanzig's

equation poses the issue of initial conditions quite clearly.

If one exploits the properties of our projector, Eq. (17), one can reduce the kinetic equation to:

$$\left(\frac{\partial}{\partial t}+\frac{1}{m}\underline{p}\cdot\frac{\partial}{\partial \underline{r}}\right) g(\underline{r},\underline{p},t) = \int_0^t d\tau\, \Sigma(\tau)\, g(\underline{r},\underline{p},t-\tau) + \text{initial value term} \qquad (19)$$

with

$$\Sigma(\tau)g = \int d^3\underline{r}' \int d^3\underline{p}' \left(\frac{\partial}{\partial \underline{p}} - \frac{1}{m}\beta\underline{p}\right) \cdot \underset{\sim}{D}(\underline{r}-\underline{r}', \underline{p}' \rightarrow \underline{p}, \tau) \cdot \frac{\partial}{\partial \underline{p}'}\, g(\underline{r}', \underline{p}'; t-\tau)$$

Let us choose the initial condition so that we have a closed, exact kinetic equation. Then, the equation is dominated by the kernel, $\underset{\sim}{D}(\underline{r}-\underline{r}', \underline{p}\rightarrow\underline{p}', \tau)$. It is non-local in space and time, and depends upon a complicated correlation of forces experienced by the test-particle. Although the equation is linear in $f(\underline{r},\underline{p},t)$, it is extraordinarily complicated, and hardly looks as though it will lend itself to a neat analysis on the basis of time scales. The 'modified propagator' exp(itQL) is particularly troublesome; one has only been able to deal with it via formal expansion of one sort or another. One knows, through example, that its properties are quite different from exp itL.

To progress systematically, one would like to expand in terms of a good, small parameter. In the case of the dense gas, we have only the familiar, inadequate pair, density and interaction strength. In lowest order, the density expansion, coupled with a time-scaling argument reproduces the simple kinetic equation for the Lorentz model. Although density expansions have received considerable attention in the test-particle problem, their effect upon the kinetic equation (19) is, for the most part, unknown. The weak-coupling expansion of $\underset{\sim}{D}(\underline{r}-\underline{r}', \underline{p}'\rightarrow\underline{p}, \tau)$ simplifies Eq. (19)

dramatically, in lowest order. The equation for a spatial Fourier component of $f(\underline{r},\underline{p},t)$ becomes:

$$\left(\frac{\partial}{\partial t}+\frac{i}{m}\underline{k}\cdot\underline{p}\right) f(\underline{k},\underline{p},t) = \int_0^t dt\, \frac{\partial}{\partial \underline{p}} \cdot \underline{\underline{D}}(\underline{k},\underline{p},\tau) \cdot \left(\frac{\partial}{\partial \underline{p}}+\frac{1}{m}\beta\underline{p}\right) f(\underline{k},\underline{p},t-\tau) \quad .$$

This has the form of a generalized Fokker-Planck equation, one in which the diffusion tensor is momentum-dependent, and has memory. It is simplest to study the case $\underline{k} = 0$, in which a spatially uniform distribution of test-particles relaxes to equilibrium, in momentum space. Then, we may write

$$\frac{\partial}{\partial t^*} f(\underline{u},t^*) = \epsilon \int_0^{t^*} d\tau \frac{\partial}{\partial \underline{u}} \cdot \underline{\underline{D}}(\underline{u},\tau) \cdot \left(\frac{\partial}{\partial \underline{u}}+2\underline{u}\right) f(\underline{u},t^*-\tau) \qquad (20)$$

where $t^* = t/t_o = \sqrt{2}\,\frac{v_o}{r_o}\,t$ is dimensionless, $\epsilon = \frac{1}{4} n r_o^3 \left(\frac{\lambda}{k_B T}\right)^2$,

$\underline{u} = (\sqrt{2}\, v_o)^{-1} \underline{v}$ is a dimensionless velocity, λ is the strength of the potential, and r_o is its range. Two time-scales appear naturally, $t_o = r_o/\sqrt{2}\, v_o$, and $t_1 = (\pi r_o^2 n \sqrt{2}\, v_o)^{-1}$. Their ratio, $\delta = t_o/t_1 = n\pi r_o^3$, has an obvious meaning. The diffusion tensor relaxes with the shorter time scale, the distribution function with the longer. The Boltzmann limit is produced if one takes the ratio of time scales to be precisely zero. Then one makes the replacement:

$$\int_0^t d\tau\, \underline{\underline{D}}(\cdot\cdot\tau) \cdot\cdot f(t-\tau) \to \left\{\int_0^\infty d\tau\, \underline{\underline{D}}(\cdot\cdot\tau)\right\} f(\cdot\cdot t) \quad .$$

and the kinetic equation is now Markovian, and familiar. However, analysis of Eq. (20) shows that as long as $\delta \neq 0$, the long-time behavior of its solutions differs from that of the Markovian equation. If this feature is not a consequence of the weak-coupling approximation itself, we have here

an example of the inter-twinedness of time scales in kinetic theory.

The next example of the generalized theory uses a more abstract setting. In fact, it approaches Koopman's original notion of setting classical mechanics in terms of the mathematics of Hilbert spaces, with benefits accruing, as in quantum mechanics. Thus, for dynamical variables A_1, A_2 selected from an appropriate space of dynamical variables, we define the inner product

$$(A_1, A_2) = \int d^3\underline{q}_1 \cdots d^3\underline{p}_N \rho_o A_1^* A_2$$

where ρ_o is the canonical distribution. Dynamical variables evolve via the action of the evolution operator $\exp itL$, so that we may write an equilibrium auto-correlation function as:

$$C_A(t) = (A, A(t)) = (A, e^{itL}A) \quad .$$

Again, projection operators play key roles. As a first example, consider the dynamical variable A, with equilibrium expectation zero, and normalized so that $(A,A) = 1$. Let $P_A = |A><A|$ project onto A, and let $Q_A = 1 - P_A$. Then, an ingenious rearrangement of the equation of motion, Eq. (9) leads to the striking form:

$$\frac{d}{dt} A(t) - i\Omega A(t) + \int_o^t d\tau\, \varphi(t-\tau)\, A(\tau) = f(t) \qquad (21)$$

where

$$i\Omega = (A, \dot{A}) = (A,\ iLA) = (A,\ PiLPA)$$

$$\varphi(t) = (f, f(t)) \quad ; \quad f(t) = e^{itQL}Q\dot{A} = e^{itQL}QiLA$$

The quantity $i\Omega$ refers to a characteristic frequency; it vanishes when A

is real in this simple example. φ is taken to describe damping, or 'memory', and $f(t)$ is interpreted as a fluctuating 'force', or as 'noise'. This rôle for $f(t)$ is sensible, for it refers only to motion in the space orthogonal to the projected (contracted) space, A. And, the equilibrium average of $f(t)$ vanishes.

Equation (21) has two valuable offspring, the equation for the auto-correlation function,

$$\frac{d}{dt} C_A(t) - i\Omega C_A(t) + \int_0^t dt\, \varphi(t-\tau)\, C_A(t) = 0 \quad , \tag{22}$$

and the equation for the evolution of the average of A, $\langle A \rangle$, with respect to an arbitrary initial distribution,

$$\frac{d}{dt} \langle A \rangle - i\Omega \langle A \rangle + \int_0^t dt\, \varphi(t-\tau)\, \langle A \rangle = \langle f \rangle \quad . \tag{23}$$

Equation (21) is a 'generalized Langevin equation'. To see more clearly, take $A = p_x$, whence $\Omega = 0$, φ is a damping with memory (frequency-dependent damping) which, in some cases becomes $\frac{\gamma}{m}\delta(t-\tau)$, and $f(t)$ has the properties necessary for the fluctuating force. Equation (22), describing the correlation function, is a closed equation, and Eq. (23) is the prototype of a kinetic equation (take $A = \delta\hat{f}_1$). In the latter case we note that the equation is closed only for certain initial distributions — a familiar point! In fact, when Eq. (23) is the equation for the average test-particle density, the corresponding Fokker-Planck equation for the distribution of density is Eq. (18).

In building a generalized kinetic theory, the dynamical variables we want to use are collective variables, not those belonging to a unique

particle. The one-body-additive functions defining mass-, momentum- and kinetic energy densities

$$\begin{pmatrix} m(\underline{r},t) \\ \underline{g}(\underline{r},t) \\ T(\underline{r},t) \end{pmatrix} = \sum_j \begin{pmatrix} m \\ \underline{p}_j \\ \frac{1}{2m} p_j^2 \end{pmatrix} \delta^3(\underline{r} - \underline{q}_j(t)) \tag{24}$$

and their Fourier components,

$$\begin{pmatrix} m_k(t) \\ g_k(t) \\ T_k(t) \end{pmatrix} = \sum_j \begin{pmatrix} m \\ \underline{p}_j \\ \frac{1}{2m} p_j^2 \end{pmatrix} e^{-i\underline{k} \cdot \underline{q}_j(t)}$$

are particularly important. Denote m_k, g_k, and T_k — adjusted to have zero expectation — as A_1, A_2, A_3. Then, it would appear profitable to project the equation of motion for each onto the three-dimensional sub-space spanned by the A's. The system which one obtains is a simple generalization of Eq. (21) and is the basis for 'generalized hydrodynamics'. The Green-Kubo relations for transport coefficients appear naturally, in this formalism, as the macroscopic limit $\underline{k} \to 0$, $t \to \infty$ is taken.

In our search for generalized Boltzmann equations the key variable is $\hat{f}_1$, itself one-body additive. The natural decomposition of its motion involves the sub-space of one-body additive functions, a space spanned by

$$N(\underline{r},\underline{p}) = \sum_j \delta^3(\underline{r} - \underline{q}_j)\, \delta^3(\underline{p} - \underline{p}_j)$$

or

$$N(\underline{k},\underline{p}) = \sum_j e^{-i\underline{k} \cdot \underline{q}_j}\, \delta^3(\underline{p} - \underline{p}_j) = |\underline{k},\underline{p}\rangle \tag{25}$$

where $(\underline{r},\underline{p})$ and $(\underline{k},\underline{p})$ are labels. We shall consider this development in some detail, focusing upon the $(\underline{k},\underline{p})$ basis. Notice first that although our bases are complete, their elements are not orthogonal. We need the results

$$B(\underline{p},\underline{p}') \equiv \langle \underline{k},\underline{p} \mid \underline{k},\underline{p}' \rangle = NM(\underline{p}') \left[\delta^3(\underline{p}-\underline{p}') + n\, M(\underline{p})\, h(\underline{k})\right]$$

$$B^{-1}(\underline{p},\underline{p}') = \frac{1}{NM(\underline{p})}\left[\delta^3(\underline{p}-\underline{p}') - n\, M(\underline{p})\, c(\underline{k})\right] \quad \text{where} \tag{26}$$

$$\int d^3\underline{p}''\, B^{-1}(\underline{p},\underline{p}'')\, B(\underline{p}'',\underline{p}') = \delta^3(\underline{p}-\underline{p}')$$

and the operator projecting into the subspace is

$$P_1 = \int d^3\underline{p}\, d^3\underline{p}'\, |\underline{p}\rangle\, B^{-1}(\underline{p},\underline{p}')\, \langle \underline{p}'| \quad . \tag{27}$$

(The index, $\underline{k}$, is suppressed, here.) The functions $h(\underline{k})$ and $c(\underline{k})$ are related to the static pair distribution function, $g(\underline{r})$. $h(\underline{k})$ is the Fourier transform of $g(\underline{r}) - 1$, and $c(\underline{k})$, the direct correlation function, is $h(\underline{k})\,[1+nh(\underline{k})]^{-1}$. Now, we may proceed to a generalized kinetic equation in either of two ways. We may choose $A = \delta\hat{f}_1(\underline{k},\underline{p}) = \hat{f}_1(\underline{k},\underline{p}) - \langle \hat{f}_1 \rangle$ as the dynamical variable, and notice that the corresponding P_A is the P_1 of Eq. (27). Then, Eqs. (21-23) apply at once, with the modification that Ω and φ are now operators with respect to momentum labels. Thus,

$$\frac{\partial}{\partial t}\delta\hat{f}_1(\underline{p},t) - i\int d^3\underline{p}'\,\Omega_k(\underline{p},\underline{p}')\,\delta\hat{f}_1(\underline{p}',t) + \int_0^t d\tau \int d^3\underline{p}'\,\varphi_k(\underline{p},\underline{p}';t-\tau)\,\delta\hat{f}_1(\underline{p}',\tau) = \cdots \tag{28}$$

and additional equations corresponding to Eqs. (22-23) tell us all that we want to know about the one-particle distribution function. The 'PiLP' aspect of $i\Omega$ is notable. It is the projected part of iL, that part of the dynamics contained entirely in the projected sub-space. We find

$$PiLP\,\delta\hat{f}(\underline{p},t) = \frac{1}{m}\underline{k}\cdot\underline{p}\,\delta\hat{f}(\underline{p},t) + k_B T n c(\underline{k})\, i\underline{k}\cdot\frac{\partial}{\partial\underline{p}} M(\underline{p}) \int d^3\underline{p}'\,\delta\hat{f}(\underline{p}',t) \qquad (29)$$

The first term represents simple streaming, and that is all one obtains in the test-particle problem. The second term reminds one of a corresponding term in Vlasov's kinetic equation for plasmas, a term describing the motion of a particle in the mean field of its neighbors. The corresponding term in the equation for fluids replaces the two-body potential by the direct correlation function, $-V(\underline{k}) \leftrightarrow k_B T c(\underline{k})$, with advantage.

[The second method, somewhat more abstract, decomposes the evolution operator, $U = e^{itL}$, and notes that the equation of motion for $P_1 U P_1 \equiv U_1$ is:

$$\left(\frac{\partial}{\partial t} - iP_1 L P_1\right) U_1(t) - \int_0^t d\tau\, iP_1 L Q_1 e^{i\tau Q_1 L Q_1} Q_1 iLP_1 U_1(t-\tau) = 0 \quad , \qquad (30)$$

closely related to Eq. (28) and its cousins, Eqs. (21-23). $P_1 U P_1$ describes the projected part of the evolution of any additive, one-body dynamical variable. It appears naturally in the autocorrelation functions for such variables. For example, $(g_k, g_k(t)) = g_k, P_1 U(t) P_1 g_k)$. Since knowledge of the equilibrium correlation function is equivalent to that of the temporal relaxation of the variable from a particular non-equilibrium state, it is customary to assert that $P_1 U P_1$ describes a kinetic equation for g_k as well.]

The memory function, $\varphi_k(\underline{p},\underline{p}';t)$ expresses dynamical correlations in scattering, and is very complicated. It must be approximated, either systematically, through expansion in a small parameter, or through 'modeling'. In any case, one would like to know as much as possible about φ_k beforehand, to ensure that an approximation that appears reasonable has not neglected some important property.

In a recent article, D. Forster has discussed general properties of φ_k, properties which should appear as 'requirements' for a sound approximation. These involve symmetries, a positivity-property, certain sum-rules, which stem from short-time behavior, and a structure that would guarantee proper approach to the hydrodynamical limit, as $\underline{k} \to 0$ and $t \to \infty$. The approach is carried out as sketched in Part I and one obtains suitably generalized expressions for transport coefficients. Since the operator $H(\underline{k})$, introduced there, is replaced by one dependent upon s as well, the approach is more delicate, and certain analyticity properties are required. Most important is that the limiting kernel ($\underline{k} \to 0$, $s \to 0$) have the five eigenfunctions of Eq. (2). This may be shown to be so for an arbitrary homogeneous isotropic classical system. It is surprising that kinetic energy appears as an eigen-function in systems of arbitrary density, but the fact is not inconsistent with conservation of energy.

V. APPROXIMATIONS TO THE MEMORY FUNCTION

The simplest approximation is surely $\varphi_k = 0$. One gets the generalized Vlasov equation, which, being collisionless, does not give sensible results in the hydrodynamic limit, although it renders short-time, i. e., high-frequency behavior correctly.

This approximation may be viewed as one in which motion orthogonal to the projected space is neglected. At once, an improvement suggests itself. Restricting the motion to S_1, the space of one-body additive variables, is too severe. Let P_1 be replaced by $P_{12} = P_1 + P_2$ which projects into S_{12}, the space of one and two-body additive functions. S_{12} may be constructed by introducing the two-body basis functions for the space S_2,

$$N(1,2) = N(\underline{r}_1, \underline{p}_1; \underline{r}_2, \underline{p}_2) = \sum_{i \neq j} \delta^3(\underline{r}_1 - \underline{q}_i)\, \delta^3(\underline{p}_1 - \underline{p}_i)\, \delta^3(\underline{r}_2 - \underline{q}_j)\, \delta^3(\underline{p}_2 - \underline{p}_j)$$

and choosing linear combinations of $N(1,2)$ that are orthogonal to the functions, Eq. (25), of S_1. Then, $S_{12} = S_1 + S_2$. The <u>form</u> of the equation of motion for $\delta\hat{f}_1$ is unaltered; only the meaning of the projectors P and Q is changed. (P_{12} is the obvious generalization of Eq. (27).) The improved approximation consists in setting $Q_{12} = 0$, whence the equation for $\delta\hat{f}_1$ becomes

$$\frac{d}{dt}\,\delta\hat{f}_1 - iL_{12}\,\delta\hat{f}_1 = 0 \quad , \quad L_{12} = P_{12}LP_{12} \tag{31}$$

Eq. (31) is Markovian, and deceptively simple. If we seek the auto correlation function for $\delta\hat{f}_1$, $(\delta\hat{f}_1, \delta\hat{f}_1(t)) = (\delta\hat{f}_1, P_1U_{12}P_1\,\delta\hat{f}_1)$, we are led at once to Eq. (30) with L replaced by L_{12} and U_1 by U_{12}. A little calculation then shows that we may replace L_{12} by L, and Q_1 by P_2 throughout. The new equation of motion

$$\left(\frac{\partial}{\partial t} - iP_1LP_1\right) U_{12}(t) - \int_0^t dt\, iP_1LP_2\, e^{i\tau P_2LP_2}\, P_2iLP_1U_{12}(t-\tau) = 0 \tag{32}$$

is unusually interesting. It is the second step in a systematic attack upon Liouville's equation. One may also view the approach as an expansion of f_N in terms of one-body, two-body, ••• functions with amplitudes given by the solutions of closed kinetic equations of increasing complexity. This promising scheme was introduced into kinetic theory by E. P. Gross and R. W. Zwanzig. It has been generalized and analyzed by C. D. Boley.

Much remains to be done as far as detailed properties of solutions of Eq. (32) "and beyond" are concerned. For example, not all of the properties described by Forster have been demonstrated for the nth order

memory function. The hydrodynamical limit has not been studied, nor have transport coefficients been calculated and judged, at any stage. However, the theory is intellectually appealing on many counts. At each stage, it is possible to eliminate the potential in favor of static correlation functions, so that the theory is in a sense 'renormalized', expressed in terms of quantities which are more accessible. In the second approximation, for example, two particles interact not in vacuum, but in the presence of a mean field due to the remaining N-2. The scheme is surely superior to direct expansion in density or coupling strength.

Gross' second approximation, though promising, does not describe the sequences of collision which lead to the singular behavior described following Eq. (13). We must refer here to another important series of papers, by G. F. Mazenko, which develop a theory of memory functions and renormalized kinetic theory. Mazenko produces tractable memory functions by truncation, and educated physical insight into the meaning of various terms. His methods lie close to those associated with 'summation of diagrams', in many-body-physics.

Mazenko's first contribution was the correct low-density memory function. This function becomes the linearized Boltzmann-Enskog kernel in the long-time ($s \to 0$) limit. [Next order in density was considered by Boley and R. C. Desai. This more complicated memory function, involving three-body collisions, gives the results of the Bogoljubov-Cohen-Green theories when appropriate limits are taken.] The low-density function for hard spheres is particularly simple. Since the collision time vanishes, φ_k is independent of s. The kinetic equation which ensues, the 'generalized Enskog equation" has been studied by Mazenko, S. Yip, and associates.

Since the equation can describe fluctuations in density of arbitrary wavelength, one can use it to understand neutron scattering data from moderately dense gases (hydrogen, and $n\pi r_o^3 < \frac{1}{100}$).

A second Mazenko-memory function, which is not limited to low densities, augments the generalized Enskog term by contributions from "ring diagrams", mode-coupling, and "cross-terms". It is designed to describe just about all interesting processes in simple classical fluids. The ring diagrams produce the divergences in the transport coeffcients and the mode-coupling terms are responsible for fluctuations near the critical point. The predictions of the model are being examined at present.

Since we have drifted from formally exact to "model" equations, we should mention the considerable success that very simple, analytical representation of the memory function have had in the interpretation (correlation?) of neutron-scattering and computer-dynamical data. The Zwanzig-Mori form of the equations of motion provides a most appropriate framework for the discussion of N-body dynamics.

To conclude this section, we return to the systematic approach to mention the earliest — the expansion in coupling parameter. The weak-coupling memory function was first deduced by A. Z. Akcasu and J. Duderstadt. The corresponding kinetic equation (accurate, one hopes, for all wavelengths and frequencies, given sufficiently small $\lambda/k_B T$) was analyzed in the original and stimulating work of D. Forster and P. C. Martin. Their discussion of the computation of η, the shear viscosity, which we shall summarize, shows the richness of the generalized method.

Kinetic theory à la Boltzmann-Landau gives

$$\eta/nk_B T = \left\langle \xi_1 \xi_3 \left| Q K^{-1} Q \right| \xi_1 \xi_3 \right\rangle$$

where K is the (weak-coupling) scattering operation. The generalized kinetic equation gives — in the hydrodynamic limit — two terms. The first,

$$\eta'/nk_B T = \langle \xi_1\xi_3 + T_{13} | QK^{-1}Q | \xi_1\xi_3 + T_{13} \rangle \ .$$

The second, $\eta''/nk_B T$, involves a matrix element of the memory function, in the $k \to 0$, $s \to 0$ limit. The new feature of η' is a contribution to the stress tensor from forces (collisional transfer), while the η'' represents an additional effect of correlations. Together, the terms modify the kinetic estimate by a factor $\left[1 + B\frac{n}{T^2} + C\frac{n^2}{T^4}\right]$.

A final remark about the systematic expansions: one wonders about their uniformity. If one uses the memory function for small $\lambda/k_B T$ or $n\pi r_o^3$, are the solutions of the approximate equations close to the exact solutions for <u>all</u> <u>k</u> and s? Or, are the approximate solutions useful only in some limit? At this point in the development of the theory, one is not sure, though some unsettling results have recently appeared in the study of a harmonic system.

SUMMARY

The power and utility of generalized kinetic theory is obvious, whether the theory is used systematically, or as a framework for modeling. In principle, it describes phenomena occurring in intervals of time and space as large or as small as one desires. In practice, it has been most successful in correlating scattering data, less so in "first principles" calculation of, say, transport coefficients. [There, description in terms of an equivalent, "classical" gas of hard spheres, augmented by data from computer experiments still satisfies the practical man.] We are in a time of rapid growth in kinetic theory. Although no formalism can mask the

difficulties inherent in 3, 4, N-body dynamics, these new tools may help us answer many questions, while minimizing headaches. Though Ludwig Boltzmann is reported to have said, "Elegance – is for tailors", I think he would be pleased.

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VI. FIGURE CAPTIONS

Fig. 1 is taken from N. K. Ailawadi, A. Rahman and R. Zwanzig, Phys. Rev. A4, 1616 (1971).

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FIGURE CAPTIONS

Fig. 1. A simple, modeled memory function is used to compute the frequency spectrum of the time correlation function for a fluctuation in density of wave number K, in liquid Argon. The dots come from computer dynamics. The solid line is 'theory'. The τ's are fitted K-dependent relaxation time.

Fig. 2. An example of the efficacy of simple, modeled memory functions in correlating neutron scattering data. The substance is liquid Argon (82.5 °K). The memory functions are Gaussian or exponential. E is the energy transfer, $\hbar Q$ the momentum transfer.

Fig. 3. The coefficient of self-diffusion in a dense gas of hard spheres is displayed, in comparison with the classical Enskog value, D_E in two situations. The solid curve is the result of computer dynamics. The points, a semi-analytical calculation based upon Mazenko's memory function. The abscissa is inversely proportional to density.

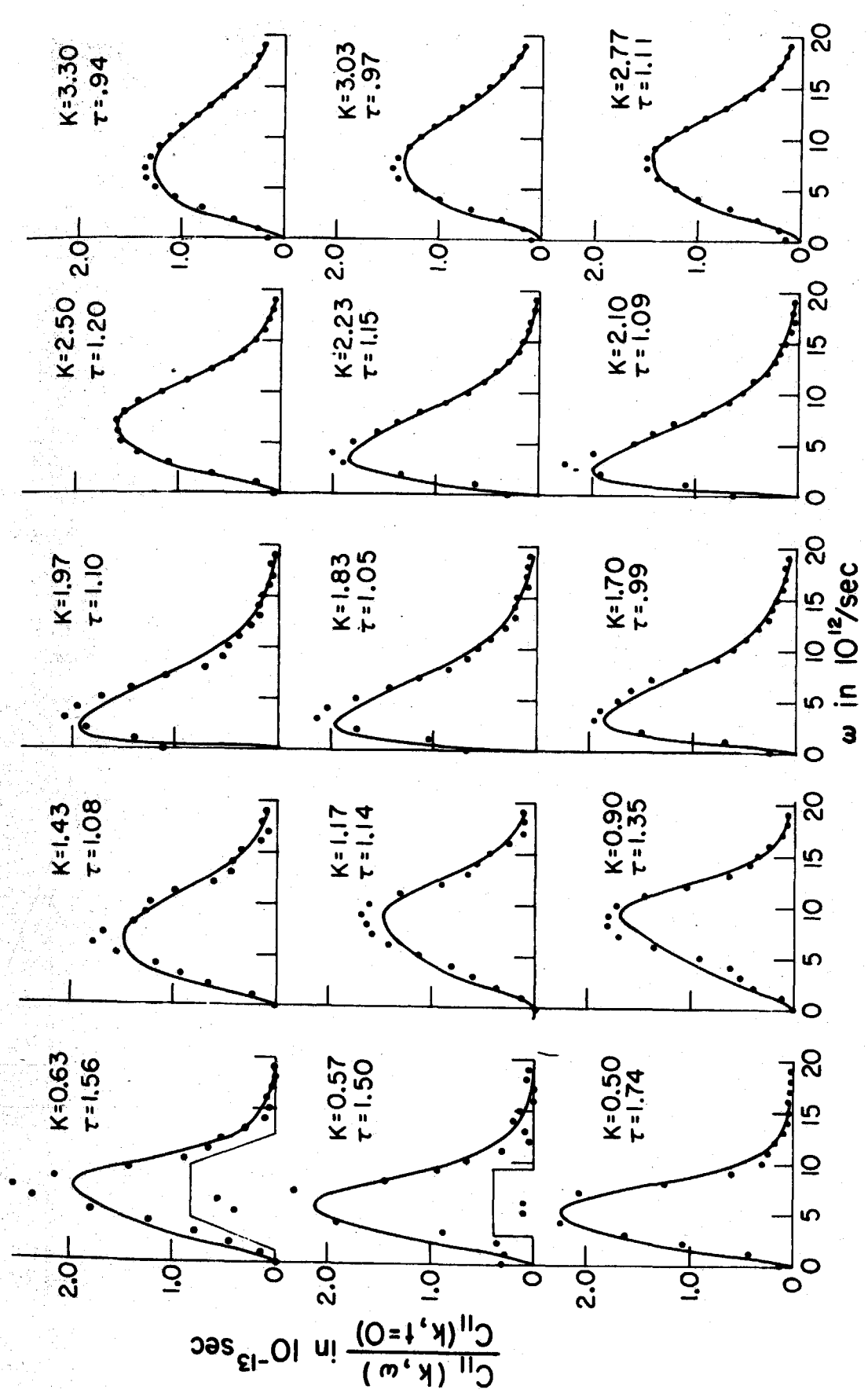
K=0.63 τ=1.56
K=0.57 τ=1.50
K=0.50 τ=1.74
K=1.43 τ=1.08
K=1.17 τ=1.14
K=0.90 τ=1.35
K=1.97 τ=1.10
K=1.83 τ=1.05
K=1.70 τ=.99
K=2.50 τ=1.20
K=2.23 τ=1.15
K=2.10 τ=1.09
K=3.30 τ=.94
K=3.03 τ=.97
K=2.77 τ=1.11
$\frac{C_{II}(k,\epsilon)}{C_{II}(k,t=0)}$ in 10^{-13}sec
ω in 10^{12}/sec

Figure 1.

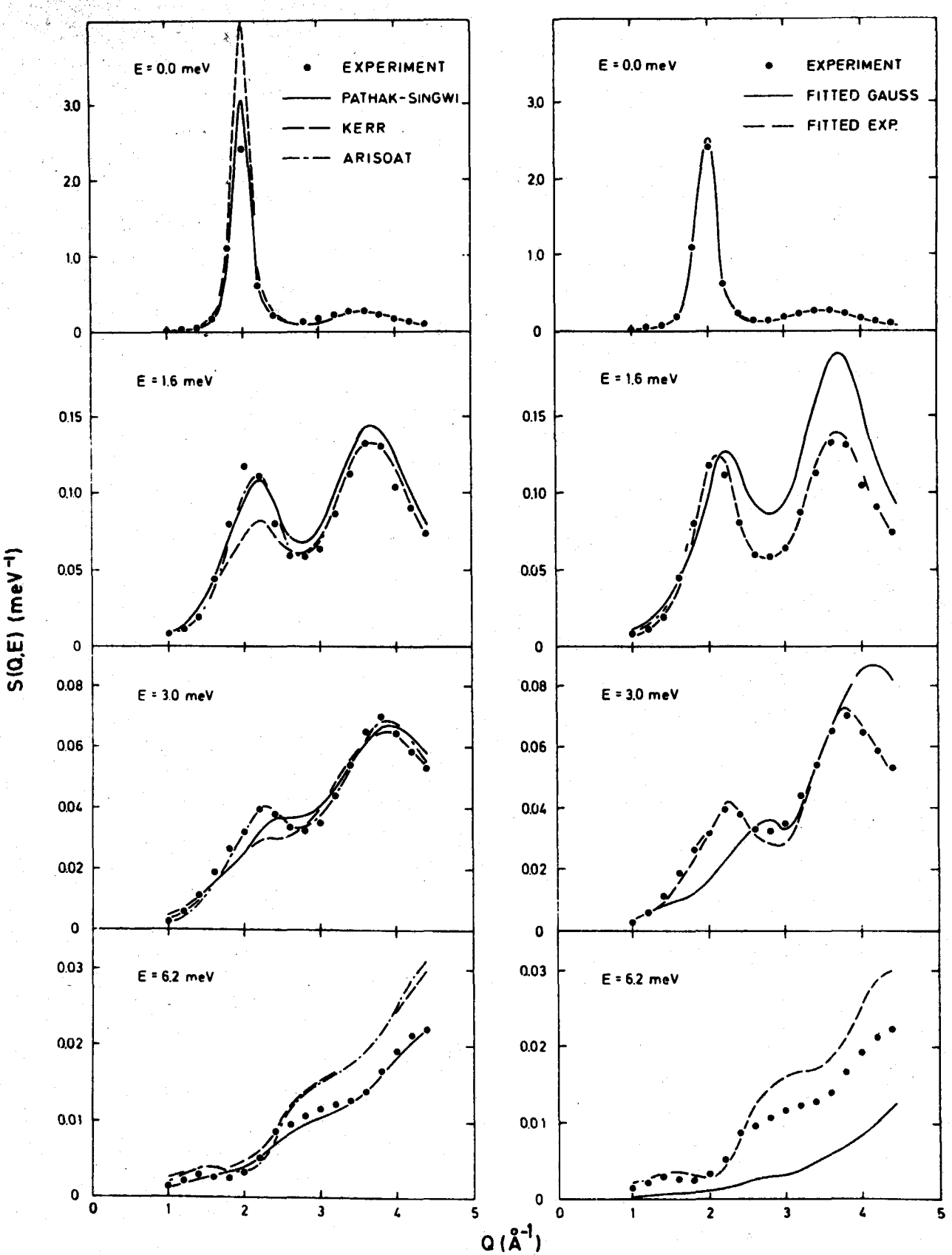
E = 0.0 meV
EXPERIMENT
PATHAK-SINGWI
KERR
ARISOAT
E = 0.0 meV
EXPERIMENT
FITTED GAUSS
FITTED EXP.
E = 1.6 meV
E = 1.6 meV
E = 3.0 meV
E = 3.0 meV
E = 6.2 meV
E = 6.2 meV
S(Q,E) (meV⁻¹)
Q (Å⁻¹)

Figure 2.

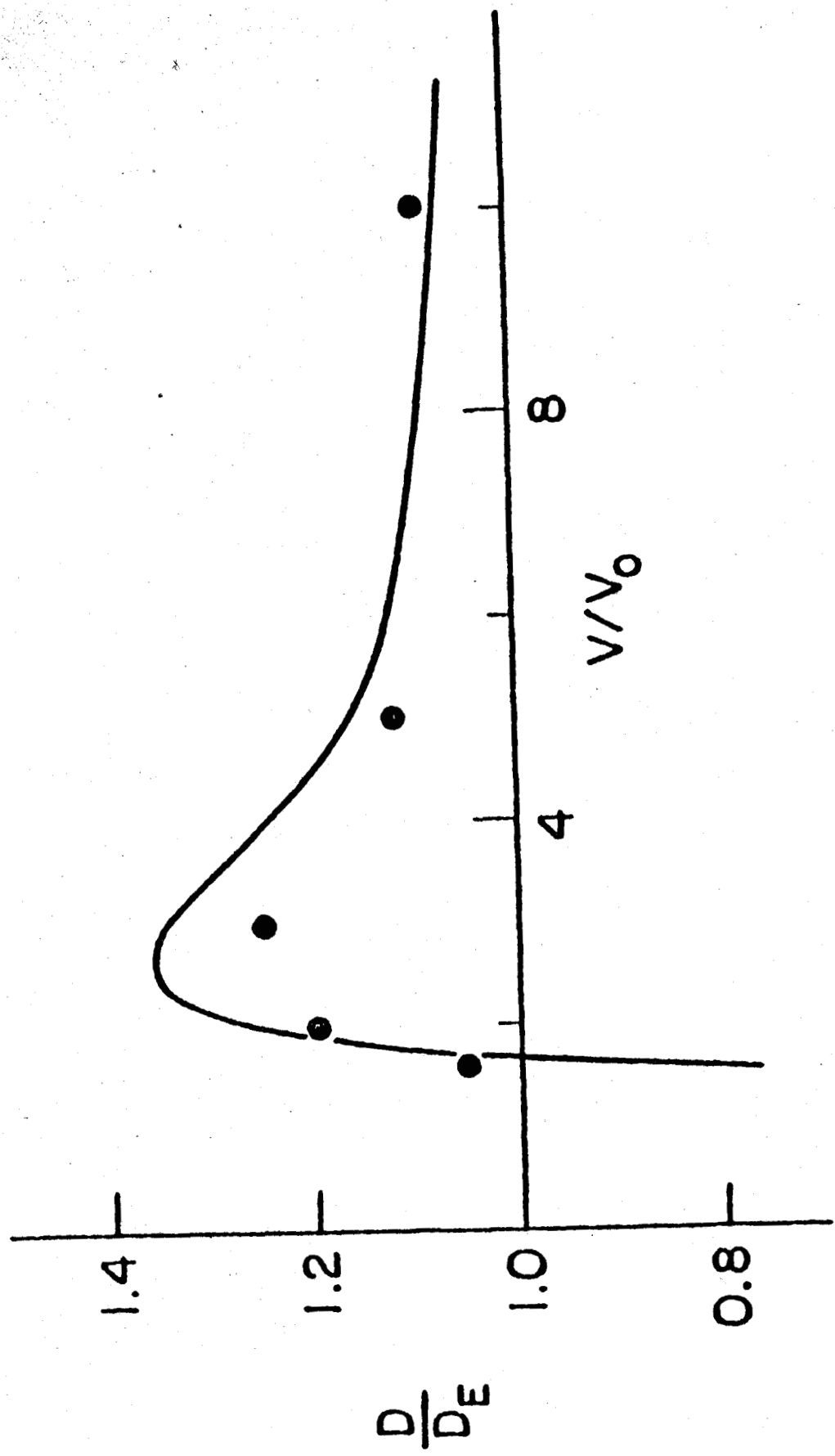

Figure 3.